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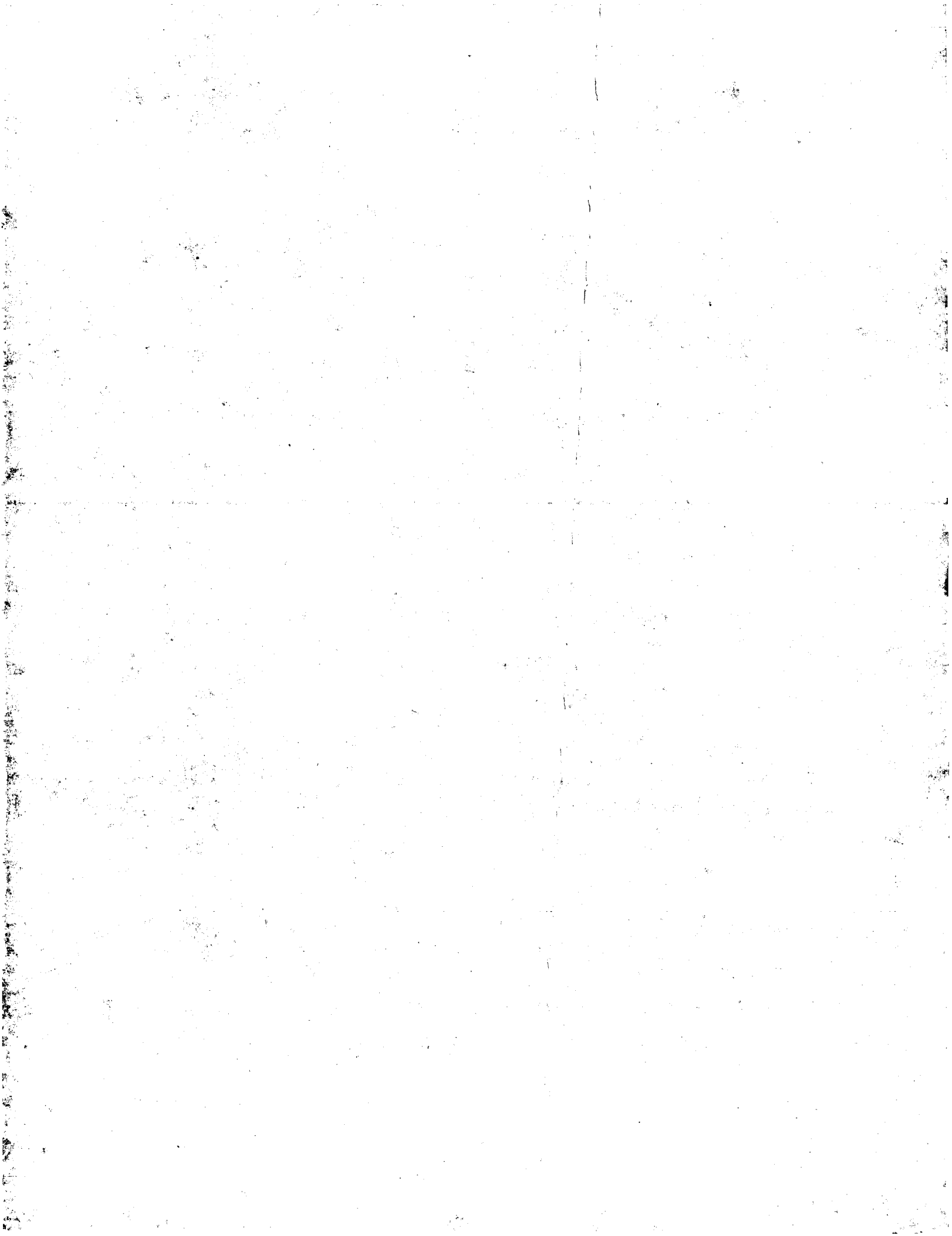
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(54) Abstract Title

Porous and voided film coatings

(57) A method for the manufacture of a porous or voided film or coating comprising application on to a substrate a water-in-oil emulsion comprising a film-forming resin, such as polyvinyl butyral, styrene/maleic anhydride copolymer, vinyl chloride copolymer, vinyl chloride/vinyl acetate/vinyl alcohol terpolymer, dissolved in a solvent. The film-forming resin is mixed with water, preferably water with a water soluble or miscible polymer, such as a salt of polyacrylic acid, and then drying the water-in-oil emulsion. The method is particularly suitable for the manufacture of heat sensitive stencils for use on stencil and/or digital duplicators.

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

Fig.1.

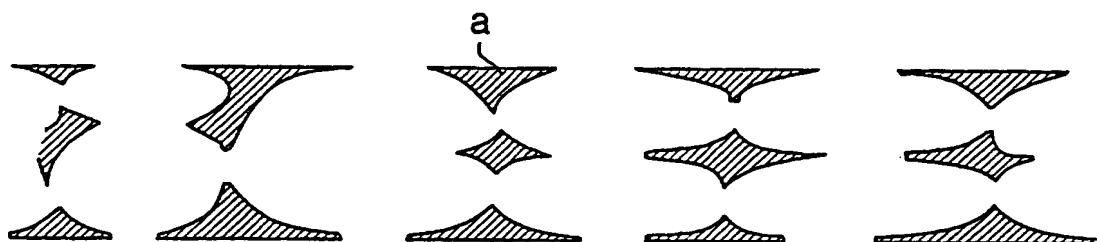


Fig.2.

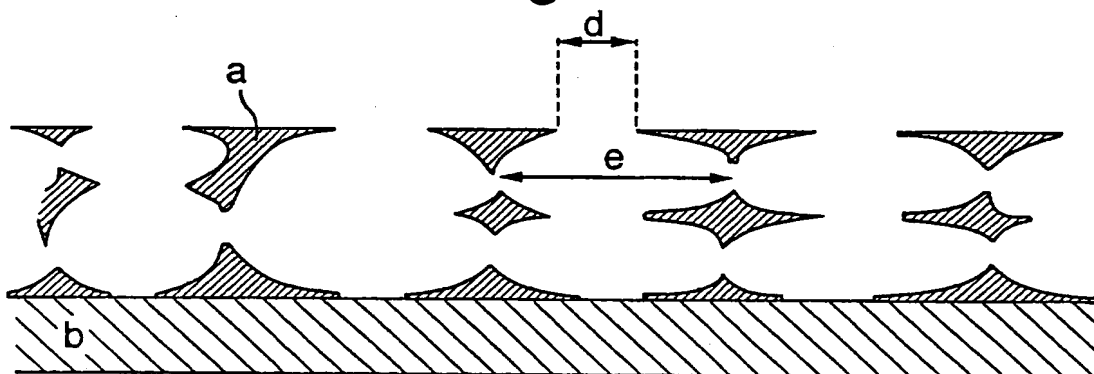


Fig.3.

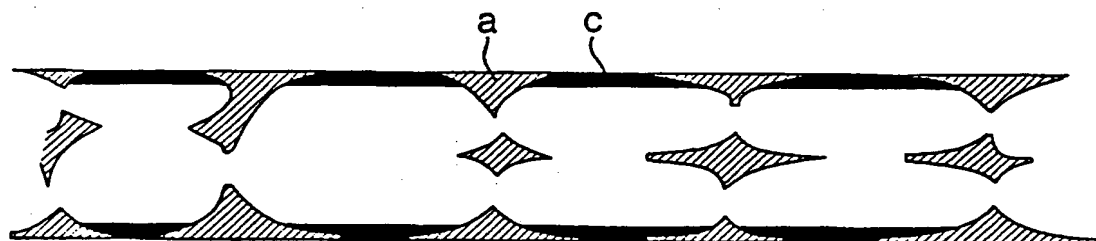


Fig.4.

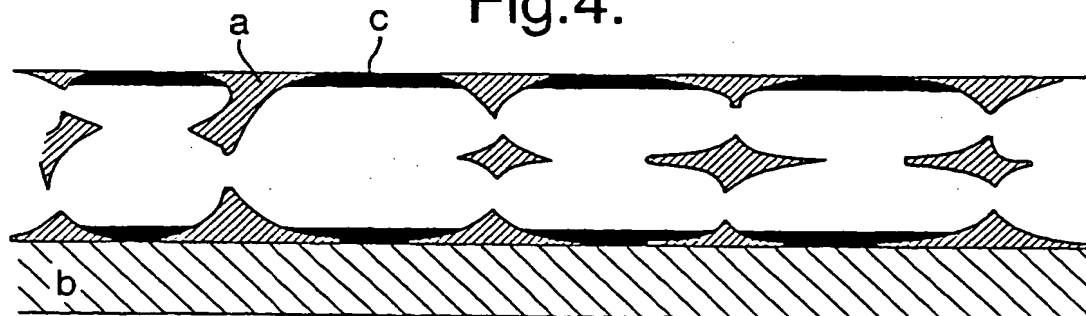


Fig.5.

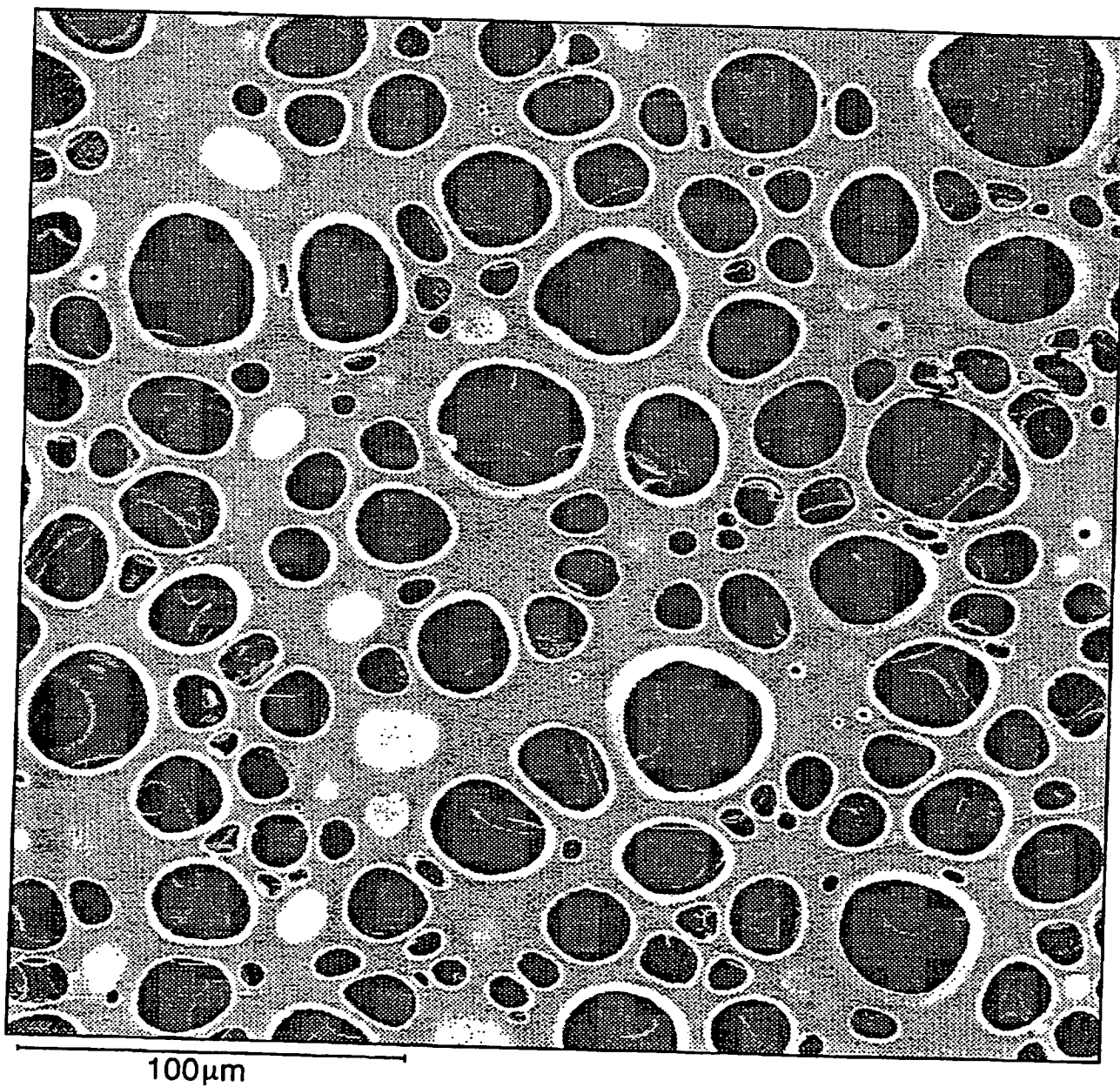
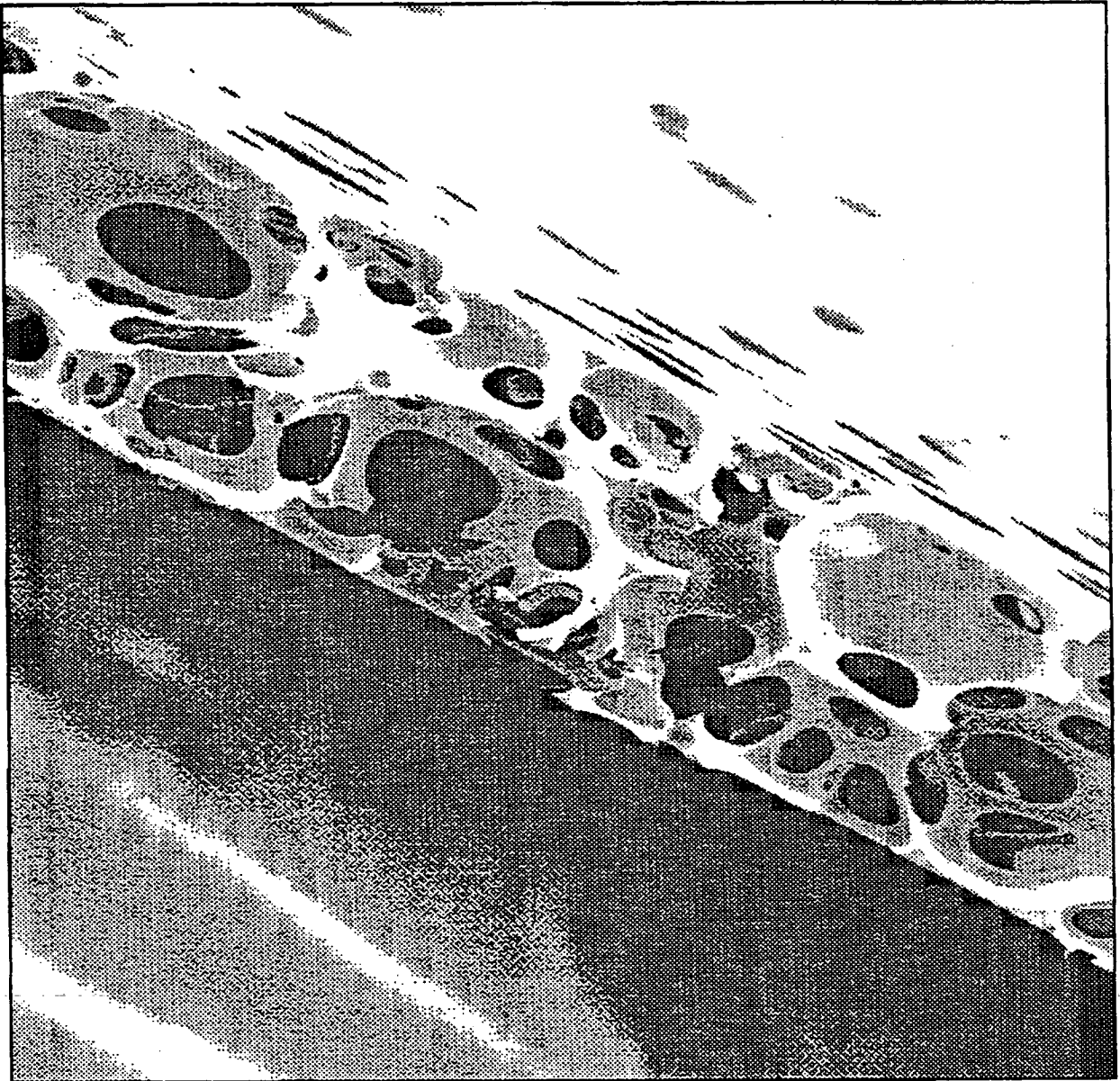


Fig.6.



POROUS AND VOIDED FILM STRUCTURESField of the Invention

5 The present invention relates to porous and voided film structures and coatings, and in particular to their use in heat-sensitive stencils of the type typically used on stencil and/or digital duplicators.

Background to the Invention

10 Heat-sensitive stencils for use on stencil and digital duplicators are required to have excellent handling, imaging and printing properties. Traditionally, heat-sensitive stencils comprise a thin, ink-permeable paper layer, typically tissue paper, bonded to a thermoplastic resin film through an adhesive. The resulting laminate is  
15 heated imagewise, for instance using a thermal head, to perforate the heated portions of the thermoplastic resin film, thereby obtaining a stencil suitable for use in printing.

20 Conventional stencils of this type have a number of disadvantages. First, the fibres in the tissue paper prevent smooth passage of ink during printing. Second, the tissue paper itself is relatively expensive. Third, the adhesive tends to accumulate in interstices between the tissue fibres, thereby preventing thermal imaging, and  
25 passage of ink during printing.

To overcome these problems, the formation of porous coatings to create heat-sensitive stencils has been suggested. For instance, GB-A-2306689 discloses a method of preparing a heat-sensitive stencil comprising dissolving  
30 a resin in a solvent blend including a first solvent capable of dissolving the resin, and a second solvent incapable of dissolving the resin and having an evaporation rate lower than that of the first solvent; applying the resulting liquid to a thermoplastic resin film; and heating  
35 to dryness. The method relies upon a change in solvent composition during the drying process. However, the method has a number of disadvantages:

(1) A very precise blend of solvents is required. Batch to batch variations in the resin e.g in molecular weight or monomer composition causes variations in solubility. As a consequence, the formulation has to be adjusted for each new manufacturing batch of resin.

(2) When water is one of the solvent components, variations in ambient water vapour levels cause variations in the pore forming process.

(3) Because solubility is temperature dependent, the temperature of the coating liquid and the drying process have to be precisely controlled.

(4) The resulting porous medium is not particularly cohesive (free standing films are not described) and incorporation of whisker mineral fillers is advocated as a means of reinforcing the structure. However, these materials can act to limit the porosity of the coating and in several instances their use raises concerns because of the potential impact on human health and safety.

#### Summary of the present invention

It has now been found that porous or voided films or coatings can be made by a method which does not suffer from the above-described disadvantages, and that this method is particularly suitable for the manufacture of heat-sensitive stencils for use in stencil and digital duplicators.

According to a first aspect of the present invention, a method for manufacturing a porous or a voided film or coating comprises

coating on to a substrate a water-in-oil emulsion comprising (i) a continuous phase which is immiscible with water and which comprises a film-forming resin dissolved in a volatile organic solvent or solvent blend, and (ii) a water phase dispersed in the continuous phase, which comprises a water-soluble or water-miscible polymer, and drying the emulsion coating.

When the substrate is a heat-sensitive thermoplastic film, e.g. a polyester, the method is suitable for manufacturing a heat-sensitive stencil. Other substrates



can be envisaged, and the method applied for the manufacture of films and coatings having widespread application, for instance as filtration media, packaging, battery separators, and so on.

5       According to a second aspect of the present invention, a method for preparing a free-standing porous or voided film comprises carrying out the method according to the first aspect of the present invention, wherein the emulsion is coated on to a release medium, and, after drying the  
10       emulsion, delaminating the resultant coating to form a free-standing film. This film can then be laminated to a thermally-sensitive thermoplastic film, to form a heat-sensitive stencil, or to any other desired substrate.

15       According to a third aspect of the present invention, a method for the manufacture of a heat-sensitive stencil comprises carrying out the method according to the first aspect of the present invention, wherein the emulsion is coated on to a release medium, after drying the coating laminating the coating to a heat-sensitive thermoplastic  
20       film, and then removing the release medium.

25       Further aspects of the present invention comprise heat-sensitive stencils produced by the above-described methods, and porous or voided films and coatings for other applications. The heat-sensitive stencils according to the present invention avoid the use of tissue paper and adhesive, and the problems associated therewith, and yet have excellent handling, imaging and printing properties.

#### Detailed Description of the Invention

30       By careful selection of the materials and conditions used in the process of the present invention it is possible to make significant variations in the properties of the resultant film or coating structure, for example its thickness, stiffness, porosity, pore volume, pore open area and, in the case of heat-sensitive stencils, adhesion to a  
35       thermoplastic film substrate. The materials and conditions suitable for use in the process of the present invention are now described in more detail.

The invention involves the use of water-in-oil emulsion comprising a continuous phase which is immiscible with water and which comprises a film-forming resin dissolved in a volatile organic solvent or solvent blend, and a water phase dispersed in the continuous phase, and which comprises a water-soluble or water-miscible polymer.

The proportion of the continuous phase to the water phase is a factor which is critical to determining the rheology of the emulsion coating and the properties of the dried coating or film. The ratio of continuous phase to water phase typically lies within the range 1:0.3 to 1:4 and preferably within the range 1:0.75 to 1:1.5.

Any film-forming resin which is soluble in the solvent or solvent blend making up the continuous phase can be used in the present invention. Typical resins include vinyl resins such as polyvinyl chloride, vinyl acetate/vinyl chloride copolymers, vinyl chloride/vinyl acetate/vinyl alcohol terpolymers, vinyl chloride/vinyl acetate/maleic anhydride terpolymers, polyvinyl acetate, and polyvinyl acetals, e.g. polyvinyl butyral; polymers and copolymers of acrylic acid esters and methacrylic acid esters; polystyrene and styrene copolymers such as styrene/maleic anhydride and acrylonitrile butadiene/styrene; polyamides; polyesters; polyurethanes; and cellulose-based resins such as cellulose acetate butyrate, cellulose acetate propionate, and ethyl cellulose. Single resins or resin blends may be used.

Preferred resins include polyvinyl acetal polymers or copolymers, and in particular polyvinyl butyral, and vinyl chloride/vinyl acetate/vinyl alcohol terpolymers, and mixtures thereof. Other preferred polymers include styrene/maleic anhydride copolymers, especially when used in combination with a polyvinyl acetal, and particularly polyvinyl butyral.

The film-forming resin is typically present in an amount of up to 30 wt.% based on the continuous phase, for instance 5 to 20 wt.%.

In addition to any physical properties that the resin contributes to the final structure, the selection of the resin component can also enhance the stability of the emulsion liquid coating.

5       The solvent or solvent blend of the continuous phase must be capable of dissolving the film-forming resin to form a phase which is substantially immiscible with water. The volatility of the solvent or solvent blend must be such that a substantial proportion, typically at least 80 wt.%,  
10       but preferably less than 100 wt. %, can be removed during the drying process before evaporation of the water phase commences. It is therefore desirable that the evaporation rate of the volatile solvent or solvent blend is greater than that of water.

15       Ethyl acetate and toluene either singly or as blends are particularly useful in the present invention, but a wide range of other solvents can also be used. When a blend of ethyl acetate and toluene is used it is believed that the drying process is not wholly sequential. Instead,  
20       some toluene may be retained by the film-forming resin at the onset of water evaporation, probably serving to plasticise the resin and thereby aid water removal. Accordingly, when the remaining toluene is removed, it is removed from a more rigid, and therefore more stable,  
25       structure than previously achieved in the prior art.

In the case of the manufacture of heat-sensitive stencils care must be exercised to ensure that the solvent does not adversely affect the thermoplastic film substrate.

30       The water phase comprises a water-soluble polymer, for example a gellant, or a water-miscible polymer. Examples of water-soluble polymers include, but are not restricted to, acrylates such as polyacrylic acid, acrylate and methacrylate esters; polyvinyl alcohol; and polyvinyl pyrrolidone. The salts of polyacrylic acid are  
35       particularly beneficial, as they function as stabilisers for the emulsion, and allow variation in the droplet size of the emulsion and thereby the pore characteristics of the

dry film. An example of a water-miscible polymer is a resin emulsion.

5 The water-soluble polymer is typically present in an amount of less than 5 wt.% based on the water phase, preferably less than 2 wt.% based on the water phase, e.g. 0.05 to 1.5 wt.%.

10 Depending upon the nature of the materials making up the continuous and water (or dispersed) phases, an emulsifying agent may be necessary to form an emulsion. However, even if an emulsifying agent is not necessary to form an emulsion, the presence of an emulsifying agent is often preferred, to enhance emulsion stability.

15 The emulsifying agent must be one which is capable of forming a water-in-oil emulsion. Examples include but are not restricted to sorbitan esters such as sorbitan mono-oleate, sorbitan trioleate and sorbitan sesqui-oleate; polymeric emulsifiers such as polyisobutene succinic anhydride amine derivative (e.g. Anfomul 2500); random copolymers of polyethylene glycol containing long-chain hydrocarbons or fatty acid components (eg. Hypermer A60);  
20 block copolymers of polyethyleneglycol and a poly(hydroxy fatty acid) (eg. Hypermer B246); and polyether substituted polydimethylsiloxanes (e.g. Abil EM97).

25 The choice of emulsifying agent affects not only the quality of the emulsion but also the process of pore formation and the properties of the final coating or film. Typically, the emulsifying agent acts to plasticise the film-forming resin and therefore the choice of emulsifying agent and its concentration has a direct effect on the  
30 stiffness of the final film structure. In some instances it is believed that the process of pore formation as the coating is dried is also aided by the emulsifying agent acting to plasticise the nearly dried resin phase and thereby to facilitate release of the occluded water  
35 component.

Release properties can be provided on the surface of the dried coating or film by the use of a silicone

emulsifying agent. This has particular benefit when the coating is to be used in roll form, as for example in the case of heat-sensitive stencils.

5 Furthermore, choice of a suitable emulsifying agent can enhance the adhesion of the coating to the substrate to which it is applied. This has particular advantages in the manufacture of heat-sensitive stencils, where the substrate is typically a thin thermoplastic film. It is believed that in such cases the emulsifying agent causes the coating  
10 liquid to achieve a degree of penetration into the surface of the film.

The concentration of the emulsifying agent is typically within the range 0.05% to 10% by weight of the total emulsion.

15 Certain film-forming resins may themselves act as an emulsifying agent, rendering the use of a additional emulsifying agent unnecessary. Examples of such resins include styrene/maleic anhydride copolymers.

20 The emulsion may also incorporate other components to provide specific effects within the manufacturing process or to achieve specific properties within the material being manufactured. These additional components, which may be contained within either phase of the emulsion, include all additives known within surface coating technology such as  
25 dyes, pigments, anti-static agents, anti-blocking agents, fillers and extenders, reinforcing and strengthening agents, release agents, dispersing agents, emulsion stabilisers, surfactants and biocides.

30 The emulsification process achieves a dispersion of the previously described water phase within the previously described continuous phase. This process may comprise direct emulsification where the water phase is added to the solvent phase or by inversion where the solvent phase is added to the water phase. Any equipment which is known for  
35 the manufacture of emulsions may be used, including but not restricted to blade and paddle stirrers, dispersing stirrers, colloid mills, and rotor stator mixers.

Emulsions with a droplet size in excess of 1  $\mu\text{m}$  are preferred for use in manufacture of the coatings or films of this invention. As a consequence lower energy methods of emulsification are preferred.

5        Coating of the water-in-oil emulsion onto a substrate can be carried out as a sheet coating method or as a continuous web coating process. Suitable coating application techniques include roller coating, knife over roll and slot-die coating. Typical coating thicknesses  
10       for stencil applications are in the range 15 to 50  $\mu\text{m}$ , preferably 20 to 35  $\mu\text{m}$ , but if desired thinner or thicker coatings may be employed. Typical coating weights for stencil applications are in the range 3 to 35  $\text{g}/\text{m}^2$ , preferably 4 to 10  $\text{g}/\text{m}^2$ , although other weights can be used  
15       according to the ultimate application of the coating or film.

When it is desired to manufacture a free-standing film the emulsion is applied to a substrate which permits subsequent release of the dried coating. Substrates which  
20       perform this function include film materials such as oriented polypropylene, silicone coated polyester, silicone coated paper, belts composed of silicone rubber or PTFE coated rubber, and steel drums with ceramic or chromium surfaces.

25       When it is desired to manufacture a heat-sensitive stencil the emulsion may be applied to a heat-sensitive thermoplastic film of the type presently used to manufacture heat-sensitive stencils which incorporate tissue paper as a porous layer.

30       Drying of the coating can be achieved by the application of heat and/or forced air. Care must be taken in the design of the drying process to ensure that the organic solvent is substantially evaporated before removal of the water commences. In the manufacture of heat-  
35       sensitive stencils, care must also be taken to ensure that the drying process has no adverse effect on the heat-sensitive film substrate. The removal of water under these

circumstances is dependent on a mass transfer drying process, in order to maintain a drying temperature which is typically below 60°C.

After drying, the coating can be annealed. Typically, annealing will be conducted for 16 to 24 hours, at a temperature in the range 30 to 50°C. The purpose of an annealing process is to achieve a material which does not exhibit undue curl even when subjected to significant changes of ambient humidity.

An alternative method for manufacturing a heat-sensitive stencil comprises laminating a free-standing porous or voided film to a heat-sensitive thermoplastic film of the type presently used to manufacture such stencils. Lamination can be carried out as a separate process from the manufacture of the porous or voided film, or directly following manufacture of the film, thus achieving an integrated process for stencil manufacture.

Suitable adhesives for use in lamination include those known to achieve lamination of polymeric media. The adhesive may be selected from solvent-borne, water-borne, and 100% solids adhesives. The adhesive may be a thermoplastic or cross-linking type. The critical limitation in selection of the adhesive is that it must not impair the quality of the laminated structure e.g. by solvent action or adhesive temperature.

Stencil manufacture by lamination has distinct advantages over a coating technique. First, higher drying temperatures can be used than in the direct coating method, where the thermal sensitivity of the thermoplastic film is a limiting factor. As a consequence:

(i) Increased coating speeds and/or more compact coating machines can be employed.

(ii) Thermal cross-linking of the porous/voided film polymer can be achieved, e.g. by inclusion of a melamine-formaldehyde resin. Such cross-linking can serve to improve the properties of the stencil e.g. tensile strength.

Second, a wider choice of resins can be used to form the porous/voided film, since it is not a requirement that the film-forming resin per se provides adhesion to the thermally-sensitive film.

5           Typically, a heat-sensitive stencil will be provided with a stickiness-preventing layer on the opposite side of the thermoplastic film substrate to the porous/voided coating or film. This layer may be applied before, after or at the same time as the porous/voided coating or film.  
10       Conventional materials can be used for this purpose. Preferably, the smoothness of that side of the film will be greater than 5,000 secs, preferably greater than 10,000 secs, as measured by using a pressurised smoothness tester supplied by Jumagai Riki Kogyo Co.

15           Heat-sensitive stencils of varying properties can be made according to the present invention, depending on the materials and process conditions selected. Typically, however, the stencils will have a stiffness in the range 5 to 200 mN, preferably 10 to 150 mN, as measured by using  
20       a Lorentzen and Wettre bending stiffness tester.

          Within the manufacturing process it is the evaporation of the water phase that creates the pores in the otherwise continuous film structure. Depending on the nature of the emulsion coating it is believed that different dried  
25       coating or film structures may be achieved. In some cases the coating or film may have open pores, i.e. pores open to the environment, or in some cases it may have closed voids, i.e. pores not open to the environment, but fully enclosed within the coating film. In the latter case, the film  
30       cover separating the voids from the environment may be so minutely thin that for all practical purposes the coating or film functions as an open pore structure. In such cases it is presumed that in performing the required function of enabling through passage of gas or liquids the applied  
35       pressure of these materials or their solvent action is sufficient to rupture immediately the thin film barrier which covers the pore entrances.



Diagrammatic representation of some of the free-standing and coated structures envisaged by the present invention is given in Figures 1 to 4.

Figure 1 shows a porous free-standing film.

5 Figure 2 shows a porous coating on a substrate.

Figure 3 shows a free-standing voided film.

Figure 4 shows a voided coating on a substrate.

10 Figures 5 and 6 are photographs of scanning electron microscopy images showing typical structures made in accordance with the present invention.

Figure 5 shows the surface of a porous film where pore diameters are typically well in excess of 10  $\mu\text{m}$ .

Figure 6 shows a cross-sectional view of a porous coating.

15 In each of Figures 1 to 4, the primary skeleton of the resulting free-standing film or coating comprises film-forming resin (a). In Figures 2 and 4, a coating is shown supported on a substrate (b). In Figures 3 and 4, a thin film cover (c) separates the pores in the film or coating from the environment. It is believed that the water-soluble or water-miscible polymer forms this thin film cover.

25 Typically, the porous and voided media made by the process of the present invention have certain characteristic features:

(1) The diameter of the pore orifices (d) is significantly less than the maximum pore dimension (e).

(2) The maximum pore dimension lies in a plane substantially parallel to the surfaces of the coating.

30 (3) There is extensive lateral interconnection of voids. When used to create heat-sensitive stencils, this feature creates an ink reservoir where the ability to have lateral movement enables very even distribution of ink on the prints which are being made.

35 As mentioned, the above techniques may be applied to the manufacture of porous or voided media other than heat-sensitive stencils.

The present invention is further illustrated by way of the following Examples.

### Examples

#### Examples 1-6

5           Table 1 gives details of coating formulations to illustrate the claims of this invention.

10           In all cases separate solvent and water phases are made by dissolution of the indicated components in the indicated phase. The emulsions are prepared by either a direct or an inversion method, as indicated, in which one phase is stirred whilst the second phase is slowly added. For preparation in the laboratory, the required emulsion droplet size can be achieved by use of a Heidolph RZR 2041 stirrer fitted with a 50 mm diameter radial flow impeller, 15 using a stirring speed of 300 rpm. On a larger scale a mixing vessel equipped with an anchor stirrer achieves comparable results.

20           Table 2 summarises results for coatings made from the formulations detailed in Table 1. The coatings were made either as wire wound rod drawdowns on a sheet substrate or by slot die coating on a continuous web. Sheet coatings were dried at 50°C in a laboratory oven. Web coatings were dried by the application of forced air at temperatures in the range of 50-57 °C.

25           In Examples 1a-c, coatings were made on oriented polypropylene film (OPP) which were subsequently delaminated to yield free-standing media. Conditions were adjusted to achieve a range of coating weights. The porosity of these coatings was measured using a Gurley Permeameter to give the results shown in Table 3.

30           TABLE 3

35

Coating Formulation Example No.	1a	1b	1c
Coating Weight g/m <sup>2</sup>	7.6	8.2	9.8
Porosity cm <sup>3</sup> /cm <sup>2</sup> /sec	41	25	20

In Examples 2 to 6, coatings were made on 2 micron heat sensitive polyester film of a type which can be used for the manufacture of heat-sensitive stencils.

5       After application of the porous coating, the uncoated side of the film was coated with a silicone based anti sticking coating of a type which has been previously described for thermal imaging stencils.

10       The resulting stencil materials were then annealed in roll form, with the anti-sticking coating on the outside, for a period of 16-24 hours at 50 °C.

The annealed stencil materials were evaluated as follows:

15       1) Stiffness was measured using a Lorentzen and Wettre bending stiffness tester.

2) Smoothness was tested using a pressurising type smoothness tester supplied by Jumagai Riki Kogyo Co.

20       3) Print density was tested using a Macbeth R914 densitometer. Test prints were made by imaging the heat sensitive stencil using a standard test pattern and printing on a Gestetner model 5380 digital duplicator at default speed. Ricoh JP6 ink filled into Gestetner CPT1 ink cartridges was used. Printing paper was Fulmar 80 g/m<sup>2</sup>. The test environment was 20-22°C at 40-60% Relative Humidity.

25       Example 7

A coating of Formulation Example No. 3 was made on silicone-coated OPP film to give a porous coating weight of 7.0 g/m<sup>2</sup> after drying.

30       A solution of moisture-curing polyurethane resin in ethyl acetate was applied to a 2 µm polyester film of a type used to manufacture thermally-sensitive stencils, to give an adhesive coat weight of approximately 0.4g/m<sup>2</sup> after evaporation of the solvent. The adhesive-coated film was  
35       then laminated to the surface of the porous coating on the silicon-coated OPP film. After delamination from the silicon-coated OPP film, the adhesive curing reaction in

5 the thin film/porous film laminate was allowed to proceed to completion. The resultant stencil was annealed and provided with an anti-stick coating as described in relation to Examples 2 to 6. The stencil had a stiffness value of 19mN, and gave a print density of 1.2 when printed on a Ricoh JP 1050 digital duplicator.

TABLE 1

EXAMPLE NUMBER		1a-c	2	3	4	5	6
Solvent Phase	Resin	Polyvinyl butyral	Mowital B30H-H				
		Styrene/Maleic Anhydride	Scripsel 540	5.20	-	-	-
		Vinyl Chloride Terpolymer	Vinylite VMCC	0.50	-	-	-
		Vinyl Chloride Terpolymer	Vinylite VAGD	-	6.90	-	-
	Emulsifying Agent	Sorbitan Mono-oleate		-	-	6.9	6.75
		Anformul 2500		-	4.00	-	-
Solvent		Abil EM97		1.80	-	4.0	4.0
		Ethyl Acetate		-	-	-	-
		Toluene		0.40	-	-	-
		Silicone Fluid DC200 5 cSt		41.40	15.6	23.5	22.95
Water Phase		Water		-	23.5	15.6	15.30
		Polyacrylic Acid, Ammonium Salt		-	-	-	1.00
Emulsification Method				51.38	49.39	49.77	50.00
				0.12	0.61	0.23	-
		Direct	Direct	Direct	Direct	Inversion	Direct

TABLE 2

Coating Formulation Example No.	1a-c	2	3	4	5	6
Sheet(s) or Web(w) Coating	Web	Web	Web	Sheet	Sheet	Sheet
Substrate	OPP	Polyester Film for Thermal Stencils				
Coating Weight g/m <sup>2</sup>	7.6 - 9.8	8.9	4.9	7.6	14.5	10.8
Stiffness mN	-	40	12	14	35	19
Smoothness secs	-	17000	15000	-	-	-
Print Density	-	1.10	1.10	1.09	1.12	0.97

CLAIMS

1. A method for manufacturing a porous or a voided film or coating comprising  
5 coating on to a substrate a water-in-oil emulsion comprising
  - (i) a continuous phase which is immiscible with water and which comprises a film-forming resin dissolved in a volatile organic solvent or solvent blend, and
  - 10 (ii) a water phase dispersed in the continuous phase, which comprises a water-soluble or water-miscible polymer, and drying the emulsion coating.
2. A method according to claim 1, wherein the continuous phase further comprises an emulsifier.
- 15 3. A method according to claim 2, wherein the emulsifying agent comprises sorbitan mono-oleate.
4. A method according to claim 2, wherein the emulsifying agent comprises a polyether-substituted polydimethyl-siloxane.
- 20 5. A method according to any of claims 2 to 4, wherein the emulsifying agent is present in an amount of 0.05 to 10 wt.% of the total emulsion.
6. A method according to any preceding claim, wherein the ratio of the continuous phase to the water phase is in the  
25 range 1:0.3 to 1:4, preferably 1:0.75 to 1:1.5.
7. A method according to any preceding claim, wherein the film-forming resin comprises polyvinyl acetal, e.g. polyvinyl butyral.
8. A method according to any of claims 1 to 6, wherein  
30 the film-forming resin comprises a styrene/maleic anhydride copolymer.
9. A method according to any of claims 1 to 6, wherein the film-forming resin comprises a vinyl chloride copolymer or terpolymer, preferably a vinyl chloride/vinyl  
35 acetate/vinyl alcohol terpolymer.

10. A method according to any preceding claim, wherein the water phase comprises a water-soluble polymer, preferably a salt of polyacrylic acid.

5 11. A method according to any preceding claim, wherein the water-soluble or water-miscible polymer is present in amount of less than 2 wt.% of the water phase.

12. A method according to any preceding claim, wherein the emulsion has a droplet size of greater than about 1  $\mu\text{m}$ .

10 13. A method according to any preceding claim, wherein the drying conditions are selected according to the nature of the volatile organic solvent or solvent blend so as to achieve removal from the emulsion of a substantial amount, e.g. at least 80 wt.%, of the volatile organic solvent or solvent blend before removal of water commences.

15 14. A method according to any preceding claim which further comprises cross-linking the film or coating, e.g. by heat treatment.

20 15. A method according to claim 1, with the proviso that the water-in-oil emulsion is not formed by mixing together either

(i) a solution of 2.5 parts by weight polyvinyl butyral resin in 28.8 parts by weight ethyl acetate, with 25 parts by weight of a 0.5% aqueous solution of methyl cellulose; or

25 (ii) a solution of 2.5 parts by weight of polyvinyl butyral resin and 0.25 parts by weight emulsifier in 28.8 parts by weight of ethyl acetate, with 20 parts by weight of a 0.5% aqueous solution of polyvinyl alcohol, preferably the polyvinyl alcohol having a saponification degree of 88%.

30 16. A method according to claim 1, with the proviso that the water-in-oil emulsion is not formed by mixing together either

35 (i) a solution of polyvinyl butyral resin in ethyl acetate, and an aqueous solution of methyl cellulose, or



(ii) a solution of polyvinyl butyral resin and emulsifier in ethyl acetate, and an aqueous solution of polyvinyl alcohol.

5 17. A method for the manufacture of a heat-sensitive stencil comprising a method as defined in any preceding claim, wherein the emulsion is coated on to one side of a thermally-sensitive thermoplastic film.

18. A method according to claim 17, wherein the drying temperature does not exceed 60°C.

10 19. A method according to claim 17 or claim 18, wherein the emulsion is coated to a thickness in the range 15 to 50  $\mu\text{m}$ .

15 20. A method according to any of claims 17 to 19, which further comprises coating on to the other side of the thermally-sensitive thermoplastic film a stickiness-preventing coating.

20 21. A method according to any of claims 17 to 20, which further comprises annealing the coated substrate for a period of 16 to 24 hours at a temperature in the range 30 to 55°C.

22. A heat-sensitive stencil obtainable by a method as defined in any of claims 17 to 21.

25 23. A heat-sensitive stencil according to claim 22, having a stiffness in the range 5 to 200 mN, preferably 10 to 150 mN.

24. A heat-sensitive stencil according to claim 22 or claim 23, which has a stickiness-preventing coating on one side thereof, the smoothness of that side being greater than 5,000 secs, preferably greater than 10,000 secs.

30 25. A heat-sensitive stencil according to any of claims 22 to 24, wherein the coating weight of the emulsion is in the range 3 to 35  $\text{g/m}^2$ , preferably 4 to 10  $\text{g/m}^2$ .

35 26. A method for preparing a free-standing porous or voided film, comprising a method as defined in any of claims 1 to 16, wherein the emulsion is coated on to a release medium, and which further comprises, after drying

the emulsion, delamination of the resultant coating to form a free-standing film.

27. A free-standing porous or voided film obtainable by a method as defined in claim 26.

5 28. A coating composition comprising a water-in-oil emulsion comprising

(i) a continuous phase which is immiscible with water and which comprises a film-forming resin dissolved in a volatile organic solvent or solvent blend and

10 (ii) a water phase dispersed in the continuous phase, and which optionally comprises a water-soluble or water-miscible polymer.

29. A coating composition according to claim 28, having the features defined in any of claims 1 to 13.

15 30. A method for the manufacture of a heat-sensitive stencil comprising laminating a free-standing film as defined in claim 27 to a thermally-sensitive thermoplastic film.

20 31. A method for the manufacture of a heat-sensitive stencil comprising carrying out a method as defined in any of claims 1 to 16, wherein the emulsion is coated on to a release medium; drying the coating; laminating the coating to a heat-sensitive thermoplastic film; and removing the release medium.

25 32. A method according to claim 30 or claim 31, wherein lamination is achieved through the use of an adhesive.

33. A heat-sensitive stencil obtainable by a method as defined in any of claims 30 to 32.



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Claims searched: 1-33

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**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:  
UK CI (Ed.R): C3C (C132); C3V (VABS, VABT, VABX, VACT, VACU, VACX)  
Int CI (Ed.7): C08J (9/28); C09D (5/02)  
Other: ONLINE: EPODOC, JAPIO, WPI.

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2306689 A RICOH, see Examples 1-2, 5, 7, 11-12.	28 at least.
X	US 5158636 A FREUDENBERG, see column 5 lines 13-15, Example 1.	1, 9, 13, 15-16, 28 at least.
X	US 4510186 A DAINICHI, see column 1 lines 50-66, column 4 lines 7-34, Examples 7-12, Claims 1 & 2.	28 at least.

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

